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Abstract

Inorganic carbon and nutrient biogeochemical responses were studied during the 2005 Pelagic Ecosystem CO_2 Enrichment (PeECE III) study. Inverse analysis of the temporal inorganic carbon dioxide system and nutrient variations was used to determine the net community stoichiometric uptake characteristics of a natural pelagic ecosystem production perturbed over a range of pCO_2 scenarios (350, 700 and 1050 μatm). Nutrient uptake showed no sensitivity to CO_2 treatment. There was enhanced carbon production relative to nutrient consumption in the higher CO_2 treatments which was positively correlated with the initial CO_2 concentration. There was no significant calcification response to changing CO_2 in *Emiliania huxleyi* by the peak of the bloom and all treatments exhibited low particulate inorganic carbon production ($\sim$15 μmol kg^{-1}). With insignificant air-sea CO_2 exchange across the treatments, the enhanced carbon uptake was due to increase organic carbon production. The inferred cumulative C:N:P stoichiometry of organic production increased with CO_2 treatment from 1:6.3:121 to 1:7.1:144 to 1:8.25:168 at the height of the bloom. This study discusses how ocean acidification may incur modification to the stoichiometry of pelagic production and have consequences for ocean biogeochemical cycling.

1 Introduction

Consequent to the increase in the atmospheric load of carbon dioxide (CO_2), due to anthropogenic release, there has been an increase in the oceanic carbon reservoir (Sabine et al., 2004). At the air-sea interface, the productive, euphotic surface ocean is a transient buffer in the process of ocean-atmosphere CO_2 equilibrium, a process retarded by the slow mixing of the surface waters with the intermediate and deep ocean, As such, the greatest changes to the CO_2 system are occurring in the surface waters. This build up of CO_2 is already altering the carbonate chemistry of the oceans and projections on decadal to centennial timescales point to changes in seawater pH (Caldiera

and Wicket, 2003; Bellerby et al., 2005; Blackford and Gilbert, 2007) and carbonate species (Orr et al., 2005) that may have ramifications for the success of organisms or whole marine ecosystems (e.g. Raven et al., 2005; Riebesell, 2005; Kleypass et al., 2006).

Exposure of phytoplankton to pH and CO_2 levels relevant to those anticipated over the coming decades leads to modifications in physiological or morphological properties which may have consequences for ecological structure and biogeochemical cycling. The general assertion is that increasing CO_2 has deleterious effects on the growth and productivity of marine calcifiers (e.g. Riebesell et al., 2000; DeLille et al., 2005; Orr et al., 2005), although there are notable exceptions (Langer et al., 2006). Overconsumption of carbon, a common response to nutrient and environmental stress is magnified under high CO_2 conditions (Zondervan et al., 2002; Engel et al., 2005). Changing CO_2 in aquatic systems has been shown to influence phytoplankton species succession (Tortell et al., 2002). Changes to the nutritional quality (higher C:P), in response to increased CO_2, of phytoplankton as a food source results in lower growth rate and fecundity in zooplankton (Urabe et al., 2003)

Efforts to understand potential consequences and feedbacks of increasing CO_2 have employed laboratory and mesocosm studies either at the individual species level or on natural and perturbed ecosystems (Riebesell et al., 2000; DeLille et al., 2005). In this study, a natural ecosystem was perturbed with nutrients over a range of atmospheric CO_2 scenarios extending previous studies to include the effects of very high CO_2 concentrations postulated for the 22nd century.

2 Methods

A mesocosm experiment was performed from 15 May and 9 June 2005 at the University of Bergen Marine Biological station in Raunefjorden, Norway. Nine polyethylene enclosures (~25 m^3, 9.5 m water depth) were moored to a raft equipped with a floating laboratory. The enclosures where filled with fjord water from 12 m depth, and ma-

nipulated in order to obtain triplicates of three different pCO_2 concentrations (1x CO_2 (350 μatm), 2x CO_2 (700 μatm) and 3x CO_2 (1050 μatm)). Addition of fresh water to the upper 5.5m of the enclosures ensured the generation of a mixed layer separated from the underlying water by a salinity gradient of 1.5. Nitrate and Phosphate were added to the upper mixed layer resulting in initial respective concentrations of 16 and 0.8 μmol kg^{-1}. A comprehensive description of the mesocosm setup, CO_2 and nutrient perturbation and sampling strategy can be found in Schulz et al. (2007). Nutrient measurement methodology is also reported in Schulz et al. (2007).

Samples for determining the carbon dioxide system were taken from seawater pumped from 1m depth in each of the enclosures. The partial pressure of carbon dioxide (pCO_2) was determined in air equilibrated with seawater pCO_2 using an infrared gas analyser (Li-Cor 6262) (Wanninkhof and Thoning, 1993). Gas calibration of the instrument against high quality air standards containing mixing ratios of 345, 415 and 1100 ppm enveloped the daily seawater measurement program. Following the pCO_2 measurements, using the same sampling methodology, samples for total alkalinity (A_T) and total dissolved inorganic carbon (C_T) were drawn into 500 ml borate bottles and immediately poisoned with $HgCl_2$. A_T was measured using Gran potentiometric titration (Gran, 1952) on a VINDTA system (Mintrop et al., 2000) with a precision of $\leq$4 μmol kg^{-1}. C_T was determined using coulometric titration (Johnson et al., 1987) with a precision of $\leq$2 μmol kg^{-1}. For both A_T and C_T measurements, samples were filtered through GF/F filters placed in the sample inlet tubes to the respective instruments immediately prior to measurement.

Calculation of additional carbon dioxide system variables used the CO2SYS program (Lewis and Wallace, 1998), from measured C_T and A_T and adopting the dissociation constants for carbonic acid (Dickson and Millero, 1987), boric acid (Dickson, 1990a) and sulphuric acid (Dickson, 1990b) and the CO_2 solubility coefficient from Weiss (1974). Seawater pH is reported on the total hydrogen scale.

Particulate inorganic carbon (PIC) production was calculated from temporal changes (Δt) in total alkalinity with appropriate correction for alkalinity contributions from net

nitrate and phosphate consumption (Goldman and Brewer, 1980):

$$\mathrm{PIC} = -0.5. \left(\frac{\left(\Delta A_T - \Delta\left[NO_3\right] - \Delta\left[PO_4\right]\right)}{\Delta t} \right) \quad (1)$$

In order to evaluate biological contributions to the inorganic carbon system it was necessary to first account for the exchange of CO_2 ($CO_{2(ex)}$) between the seawater and the overlying mesocosm atmosphere. Gas exchange was calculated according to Delille et al. (2005) further employing the chemical enhancement factors of Kuss and Schneider (2004).

Net community production (NCP) was calculated from temporal changes in C_T allowing for modifications due to PIC production or dissolution and net CO_2 gas exchange thus:

$$\mathrm{NCP} = -\left(\frac{\Delta C_T}{\Delta t} \right) + 0.5. \left(\frac{\left(\Delta A_T - \Delta\left[NO_3\right] - \Delta\left[PO_4\right]\right)}{\Delta t} \right) + \frac{CO_{2(ex)}}{\Delta t} \quad (2)$$

Removal of the contributions of net calcification and air-sea CO_2 exchange gives the net perturbation of the inorganic carbon system from community biological activity – the sum of autotrophic and heterotrophic processes within the mixed layer. Comparison of the inferred net organic production and nutrient uptake rates gives the pelagic community molar stoichiometry changes as a response to changing CO_2.

3 Results

3.1 Temporal evolution of the carbon dioxide system

In accordance with the agreement for the PeECE special issue, only treatment means are represented in this study and not the results from individual mesocosm bags. Daily treatment means, with standard deviations, of seawater partial pressure of carbon dioxide (pCO_2), total inorganic carbon (C_T) and nutrient concentrations for the mixed layers

in the three perturbation scenarios are shown in Fig. 1. The concentrations for each variable (Day 1) illustrate only the response of the mesocosms to the initial nutrient and carbon dioxide modifications following the CO_2 charging and nutrient additions as detailed in Schulz et al. (2007) and, consequently, the starting date for the present study, when the mesocosms reached a "steady state" was determined to be day 2.

Once the scenario CO_2 concentrations had been reached in the seawater, only the atmospheric concentrations over the water were maintained at the prescribed treatment level and the seawater CO_2 system was allowed to respond to processes as in a naturally occurring plankton bloom. There is a clear treatment dependant response in pCO_2 (Fig. 1a). Under the 1x CO_2 scenario, pCO_2 dropped by 202 μatm by the end of the bloom stage (Day 12), whilst pCO_2 reductions were 335 and 570 μatm in the 2x and 3x CO_2 scenarios, respectively. Similarly, the C_T reductions also show the same order of response (Fig. 1b). Under the 1x CO_2 treatment, C_T showed a reduction of 94 μmol kg^{-1}, increasing to 107 μmol kg^{-1} and to 118 μmol kg^{-1} as the CO_2 treatment increases. Initial concentrations of A_T (Fig. 1c) were higher in the 3x CO_2 treatment corresponding with the higher initial salinity (Schulz et al., 2007). Changes in A_T throughout the bloom stage indicated a modest treatment response before Day 10 with reductions in A_T of 21, 23.5 and 24.8 μmol kg^{-1} (1x CO_2 through 3x CO_2 treatments). Total alkalinity increased after the bloom peak in the 2x and 3x CO_2 treatments but remained constant in the 1x CO_2 treatment.

The absolute change in carbonate ion [CO_3^{2-}] concentrations, on the other hand, showed no treatment dependence and increased by 50, 52 and 49 μmol kg^{-1} in the low to high treatments, respectively (Fig. 2a). Correspondingly, as Ω is controlled mainly by [CO_3^{2-}], there were similarly increases in the calcite saturation state; 1.2, 1.27 and 1.19 (Fig. 2b). Seawater pH (pH_T) values, however, increased the most in the 3x CO_2 treatment from 7.64 to 7.96 (ΔpH=0.32); under the 2x CO_2 scenario the pH increased from 7.81 to 8.07 (ΔpH=0.26) and in the 1x CO_2 treatment from 8.11 to 8.27 (ΔpH=0.16).

Particulate inorganic carbon (PIC) production showed a similar response under all CO_2 treatments (Fig. 3a). The dominant calcifier in the bloom was the prymesiophyte

Emiliania Huxleyi (Paulino et al., 2007) and PIC production increased to a maximum of 15 μmol kg^{-1} on Day 10 corresponding to the start of the demise of the *Emiliania Huxleyi* population (Paulino et al., 2007). Cumulative PIC remained constant in the 1xCO_2 treatment until the end of the experiment suggesting no significant calcification or dissolution. However, in the higher CO_2 treatments cumulative PIC decreased slowly due to either increased dissolution or input of A_T from below (Schulz et al., 2007).

Net community production (NCP) (Fig. 3b), the net organic carbon production, contributed the most to the changes in inorganic carbon dioxide shown in Fig. 1b with contributions from PIC and air-sea CO_2 exchange (not shown) of only 15–20% to the C_T changes. The cumulative NCP has a maximum on Day 12 and shows a clear treatment response with maximum production, relative to Day 2. The 3x CO_2 treatment produced 110 μmol kg^{-1}, falling to 96μmol.kg-1 and 80 μmol kg^{-1} in the 2x CO_2 and 1x CO_2 treatments. After Day 12 there is a fall in calculated NCP. It was not possible to ascertain the relative influence of respiration and the response to a storm – mixing of water, higher in CT, from below the halocline (Schulz et al., 2007), followed by further treatment divergence in NCP until the end of the experiment - again favouring the 3x CO_2 treatment.

3.2 Temporal evolution of nutrients

The treatment dependant changes in the major nutrients nitrate, phosphate and silicate are shown in Fig. 1c–e. Both nutrient uptake and the timing of nutrient minima showed no significant dependency on CO_2 treatment although there were inter-treatment variations in the planktonic assemblages (Paulino et al., 2007). Silicate was not added during the experimental set-up, however a residual concentration of about 3 μmol kg^{-1} was inherited from the fjord water used to fill the mesocosm enclosures. Silicate concentrations dropped sharply due to diatom uptake and reached a minimum on day 9–10. Phosphate concentrations showed only modest reductions until day 5 after which rapid uptake led to a minimum on day 11. From the onset of the experiment, concentrations of nitrate diminished at a steady rate until Day 12 then declined slowly until the

end of the experiment..

The stoichiometry of net community inorganic nutrient to calculated organic carbon uptake is shown in Fig. 4. As expected, with the measured nutrient concentrations exhibiting no scenario dependence, there is little significant deviation in nutrient stoichiometry between treatments. In the pre-bloom period, until day 5, there is a greater uptake of nitrate to phosphate relative to the Redfield ratio (16:1) (Redfield et al., 1963). In the initial stage of the bloom, relative phosphate uptake increases rapidly on Day 6. Thereafter, the system behaves very close to Redfieldian until the end of the bloom when N/P rose slowly to a final cumulative value of 21 in all treatments.

Nitrate uptake is high compared to silicate uptake until Day 4, after which the diatom bloom started (Paulino et al., 2007) and silicate was consumed at about 1:1 with nitrate until silicate reached a first minimum on Day 7. There followed a small peak in silicate concentration on Day 8 (Fig. 1f) after which silicate became depleted on Day 9–10.

In contrast to the nutrient stoichiometric ratios, there are significant treatment dependant differences between the carbon to nitrate (C/N) (Fig. 4c, g) and carbon to phosphate (C/P) ratios (Fig. 4d, h). Overconsumption of carbon results in a higher C/N under higher CO_2 exposures. Cumulative C/N uptake was higher in the 3x CO_2 scenario throughout the entire bloom, quickly reaching a peak of 7.5–8.25 by Day 6 and remaining at this level until Day 12. The pre-bloom responses in the 1x and 2x CO_2 treatments were similar until day 5 after which the 2x CO_2 treatment increased C/N uptake to 7.1. A similar order of response was seen in the C/P ratio with the 3x treatment showing a greater carbon overconsumption throughout the experiment. In contrast to the C/N response, the C/P increased significantly in the post-bloom phase.

4 Discussion

4.1 Modification of the carbonate system

As changes to A_T (including contributions from nutrient alkalinity) were similar and low and gas exchange minimal in all treatments, modifications to C_T were mainly due to organic carbon production. As such, the greatest changes were related to the treatment dependant carbon overconsumption with increasing uptake with increasing initial pCO_2. The effect on pCO_2 due to the greater carbon uptake is exacerbated due the low buffer capacity of the high CO_2 seawater resulting in a rapid reduction of pCO_2 in the 3x CO_2 treatment. The opposite response is seen with pH_T with the largest increases found in the 3x CO_2 scenario. Due to the weakly buffered system in a future ocean, pelagic ecosystems will undergo greater seasonal changes in their ambient CO_2 fields. Increasing CO_2 will reach a point where changes to the carbonate system will move outside the contemporary "carbonate system envelope": in this experiment, at no point did any of the calculated carbonate system variables in the 2x CO_2 and 3x CO_2 treatments overlap with the range of the 1x CO_2 scenario.

4.2 Calcification

There has been shown to be a response to the saturation state of $CaCO_3$ ($\Omega_{calcite}$) in seawater and the growth and health of many calcifying marine organisms (e.g. Reibesell et al., 2000; Langdon et al., 2003; Kleypass et al., 2006; DeLille et al., 2005; Langer et al., 2006). The dominant calcifier during the experiment was the prymesiophyte *Emiliania Huxleyi* which is common to the Norwegian fjords and open waters of the Norwegian and Barents Sea. Calcification in *Emiliania Huxleyii* has been shown to be controlled by light, nutrient (especially phosphate) and carbonate ion concentrations and calcite saturation state (see review in Zondervan, 2007). The photon flux density (PFD) concentrations throughout the experiment (Schulz et al., 2007) always exceeded the threshold for saturation of 150–300 μmolphotons m^{-2} s^{-1} found by

Nielsen (1997) and Zondervan et al. (2002) and therefore it is assumed that there was no light limitation on calcification. In this study there was no treatment difference in nutrient utilisation although the concentrations of *Emiliania Huxleyii* varied between treatments (Paulino et al., 2007). Merico et al. (2006) postulated that the seawater carbonate ion concentration could be a control on the onset of calcification and Delille et al. (2005), showed that calcification was delayed by 1 day during a 2x CO_2 treatment compared to the contemporary treatment. This study does not find any relationship between $[CO_3^{2-}]$ and the timing or degree of calcification. Further, although the $[CO_3^{2-}]$ and $\Omega_{calcite}$ values showed marked inter-treatment variations throughout the experiment there was no difference in cumulative net community calcification by the peak of the bloom. This varies from the results of DeLille et al. (2005) who reported a 40% reduction in PIC production between 1x CO_2 and 2x CO_2 treatments. Conversely, this study does not show the promotion of higher calcification with increasing CO_2 as found by Langer et al. (2006). The concentrations of *Emiliania Huxleyii* are much lower in this study (Paulino et al., 2007) than in Delille et al. (2005) experiment. It may be that the subtle inter-treatment differences in PIC production seen before Day 12 (Fig. 3a) would magnify to be significant within a plankton bloom dominated by *Emiliania Huxleyii*.

4.3 Carbon consumption and nutrient stoichiometry

Elemental stoichiometry of biological production in the surface ocean controls, to a great extent, nutrient balance and cycling of the global ocean. Ocean nutrient stoichiometry is controlled on short timescales by the resource allocation in marine organisms (e.g. Redfield, 1958; Klausmeier et al., 2004) and on longer scales by continental nutrient supply (Broecker, 1982). The degree of efficiency of the connectivity between the surface and interior ocean is also controlled by the stoichiometry of sedimentary In this work, molar stoichiometric nutrient uptake ratios are inferred from the uptake of dissolved inorganic nutrients and thus reflect the community balance at a particular time. This method, therefore, cannot discriminate species specific uptake as suggested by Klausmeier et al. (2004) but may be used to characterise distinct patterns in community

nutrient balance under differing CO_2 regimes.

Overconsumption of carbon relative to nutrient supply has been reported in several studies of the planktonic response to increased CO_2 (Riebesell et al., 1993, 2000; Banse, 1994; Delille at al., 2005; Engel et al., 2005) The increase in carbon uptake is usually seen at the end of the bloom suggested to result from TEP production in response to nutrient stress (Engel et al., 2002, 2004). Hein and Sand-Jensen reported an immediate (2h) increase in primary production in relation to increased CO_2 concentrations. Changes in dissolved aqueous CO_2 may determine the phytoplankton cell size distribution (Engel et al., 2007). Egge et al. (2007) also reported increased primary production, based on in situ ^{14}C incubations, in this study in the higher CO_2 treatments towards the peak of the bloom. However, the overconsumption derived from chemical uptake estimations is seen from the onset of the experiment and is proportional to the initial treatment CO_2 concentration (see also Riebesell et al., 2007). As Schulz et al. (2007) report no changes to the stoichiometry of dissolved and particulate organic matter, this implies that there was most likely an increase in the carbon exported from the mixed layer relative to nutrient concentration in the high CO_2 treatments.

4.4 Consequences for ecosystem functioning, ocean biogeochemical cycling and atmospheric CO_2 control

The elemental stoichiometry of biological export has an important role in controlling atmospheric CO_2 concentrations (Broecker, 1982; Volk and Hoffart, 1985; Omta et al., 2006). From first principles, the stoichiometry of osmotroph uptake is transferred to the standing stock of pelagic production. Non-redfield signatures of biological production have been documented in the surface ocean (Sambrotto et al., 1993; Anderson and Sarmiento, 1994; Falck and Anderson, 2005; Koeve, 2006) and at depth (Kortzinger et al., 2001; Pahlow and Riebesell, 2000). This study has indicated an increase in the carbon:nutrient stoichiometry of pelagic osmotroph productivity in a high CO_2 world. If the PeECE results are representative of global productivity, with an efficient transfer of this carbon overconsumption to depth, the increase in atmospheric CO_2 increase by the

end of the century may be reduced by 58 μatm (Riebesell et al., 2007). The efficiency of carbon-nutrient perturbations in the upper ocean on atmospheric CO_2 depends on the rate and ultimate depth of sedimentation which has been shown to be significantly controlled by the ballast of the sedimenting material (Klaas and Archer, 2002). The ballast is mainly dependant on the proportion of $CaCO_3$ to particulate organic carbon ($CaCO_3$:POC) and has been used to test the sensitivity of changes to the carbonate pump on atmospheric CO_2 (Heinze, 2003; Ridgwell et al., 2007). Previous studies have identified a reduction in the calcification rate of pelagic calcifiers (summarised in Ridgwell et al., 2007). Calcification was insensitive to CO_2 level in this study and Schulz et al. (2007) show that there was increased export of organic carbon from the mixed layer under the 3x CO_2 treatment, suggesting a lowering of the ballast effect. This would suggest that the atmospheric control proposed by Riebesell et al. (2007) would be diminished if there were no compensatory processes to offset the reductions in the ballast effect. However, Engel et al. (2007) show that there was an increase in the cell size during the PeECE II experiment. This cell size change with increases in TEP production and, thus potentially higher aggregation of particulates shown to be a response of similar pelagic plankton communities (Engel et al, 2002; 2004), may be a mechanism to increase sedimentation rates in a high CO_2 environments.

Carbon overconsumption by osmotrophs changes the nutritional quality of food for zooplankton. Lower growth, productivity and fecundity has been documented in zooplankton fed on phytoplankton grown under high CO_2 (Sterner and Elser, 2002; Urabe et al., 2003,; Anderson et al., 2005). Carotenuto et al. (2007) hypothesise that the high C:N uptake during the PeECE III study reduced recruitment of zooplankton nauplii. Changes to the ecological structure of pelagic community will also control the export of stoichiometric signals through changes to the size structure and ballast of sedimenting material.

There exists now a large array of experimental data, from laboratory and mesocosm studies of individual species and ecosystem studies, on ecological and biogeochemical responses to ocean acidification. The requirement now is for detailed statistical meta-

analysis to breakdown the complexity and often contradiction, to identify the dominant controls and responses to ocean acidification. With this information, the observationalists and modellers, presently identifying large contemporary changes in the oceanic carbon sinks (e.g. Schuster and Watson, 2007; Canadell et al., 2007), will be able to focus efforts on the oceanic processes sensitive to changes in the CO_2 system.

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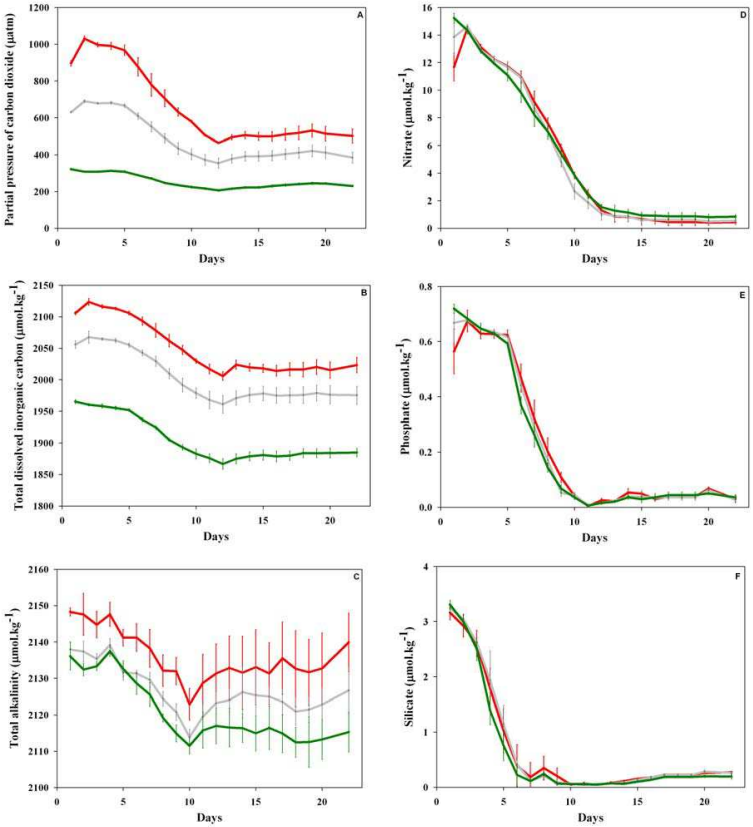

Fig. 1. Temporal development of the carbon dioxide variables and nutrient concentrations within the mesocosm upper mixed layers: **(A)** partial pressure of carbon dioxide; **(B)** total dissolved carbon dioxide; **(C)** Total alkalinity; **(D)** Nitrate; **(E)** Phosphate; and **(F)** Silicate. The mean treatment values (350, 700 and 1050 μatm), with standard deviation, are represented by the green, grey and red lines, respectively.

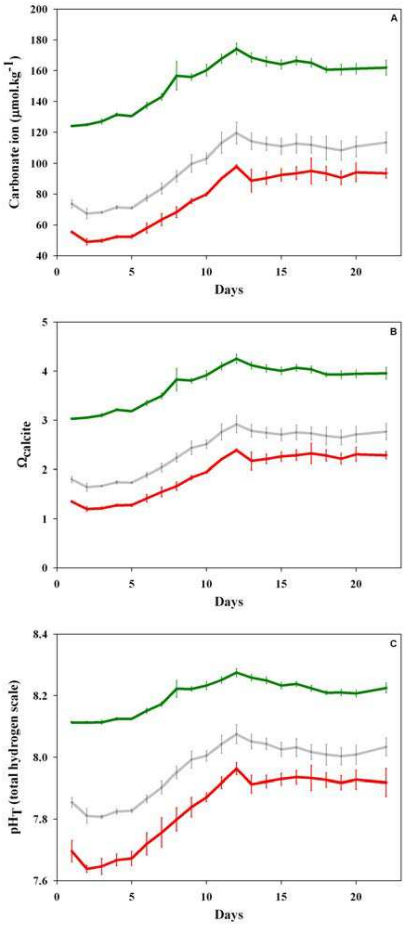

Fig. 2. Calculated carbon dioxide system variables within the mesocosm upper mixed layers: **(A)** Carbonate ion concentration; **(B)** saturation state of calcite (Ω); and **(C)** pH_T. The colour assignment of treatment is as in Fig. 1.

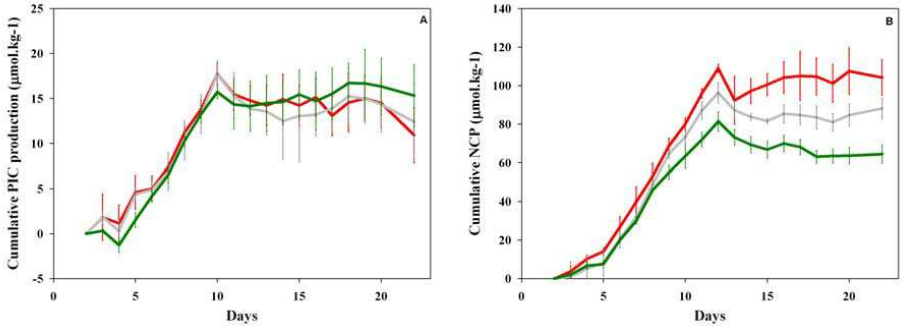

Fig. 3. The main contributors to changes in the inorganic carbon concentration throughout the experiment **(A)** Cumulative particulate inorganic carbon (PIC) production and **(B)** net community production (NCP). The contribution of CO2 air-sea gas exchange to the net CT change was small (<1%) and not shown. The colour assignment of treatment is as in Fig. 1.

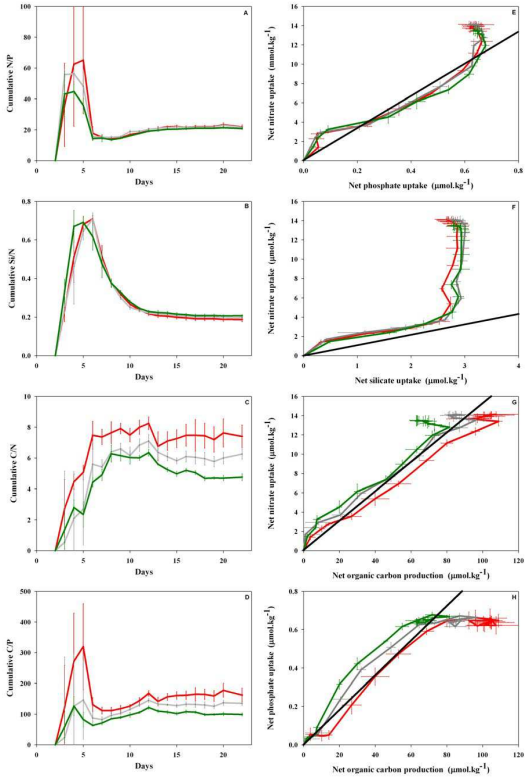

Fig. 4. Net community nutrient stoichiometric uptake ratios referenced to Day 2. Illustrated are the respective daily changes and parameter-parameter relationships for nitrate to phosphate **(A, E)**; silicate to nitrate **(B, F)**; organic carbon to nitrate **(C, G)**; and organic carbon to phosphate **(D, H)**. The black line represents the conventional Redfield ratio (Redfield et al., 1963) (E, G, H) and a silicate-nitrate relationship of 0.95:1 from the mean of diatom species Si/N reported in Table 3 of Brezinski (1985) (0.95:1±0.4) (F). The colour assignment of treatment is as in Fig. 1.

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